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<b>(21) International Application Number:</b> PCT/FI00/00409 <b>(22) International Filing Date:</b> 9 May 2000 (09.05.00) <b>(30) Priority Data:</b> 991069 10 May 1999 (10.05.99) FI <b>(71) Applicant (for all designated States except US):</b> BOREALIS TECHNOLOGY OY [FI/FI]; P.O. Box 330, FIN-06101 Porvoo (FI). <b>(72) Inventors; and</b> <b>(75) Inventors/Applicants (for US only):</b> GAROFF, Thomas [FI/FI]; Borgströminkuja 4 K 104, FIN-00840 Helsinki (FI). LEINONEN, Timo [FI/FI]; Massatie 8, FIN-06750 Tolkkinen (FI). <b>(74) Agent:</b> BERGGREN OY AB; P.O. Box 16, FIN-00101 Helsinki (FI).		<b>(81) Designated States:</b> AE, AG, AL, AM, AT, AU, AZ, BA, BB, BG, BR, BY, CA, CH, CN, CR, CU, CZ, DE, DK, DM, DZ, EE, ES, FI, GB, GD, GE, GH, GM, HR, HU, ID, IL, IN, IS, JP, KE, KG, KP, KR, KZ, LC, LK, LR, LS, LT, LU, LV, MA, MD, MG, MK, MN, MW, MX, NO, NZ, PL, PT, RO, RU, SD, SE, SG, SI, SK, SL, TJ, TM, TR, TT, TZ, UA, UG, US, UZ, VN, YU, ZA, ZW, ARIPO patent (GH, GM, KE, LS, MW, SD, SL, SZ, TZ, UG, ZW), Eurasian patent (AM, AZ, BY, KG, KZ, MD, RU, TJ, TM), European patent (AT, BE, CH, CY, DE, DK, ES, FI, FR, GB, GR, IE, IT, LU, MC, NL, PT, SE), OAPI patent (BF, BJ, CF, CG, CI, CM, GA, GN, GW, ML, MR, NE, SN, TD, TG).  <b>Published</b> <i>With international search report. Before the expiration of the time limit for amending the claims and to be republished in the event of the receipt of amendments.</i>
<b>(54) Title:</b> CATALYST COMPONENT COMPRISING MAGNESIUM, TITANIUM, A HALOGEN AND AN ELECTRON DONOR, ITS PREPARATION AND USE		
<b>(57) Abstract</b> <p>The invention relates to a process for the preparation of an olefin polymerisation catalyst component, said catalyst component and its use. The process is mainly characterised by the steps of: (i) reacting in solution a magnesium compound containing an alkoxy group, a carboxylic acid halide and a four-valent titanium compound containing a halogen, for obtaining a dissolved reaction product and (ii) recovering a fraction of the reaction product from step (i) in particulate form by contacting the dissolved reaction product with a mixture of an aromatic and an aliphatic hydrocarbon, or by contacting the dissolved reaction product first with an aromatic hydrocarbon and then with an aliphatic hydrocarbon, the amount of aromatic and aliphatic hydrocarbon being at least 5 mol per mol of magnesium.</p>		

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**Catalyst component comprising magnesium, titanium, a halogen and an electron donor, its preparation and use**

5 The invention relates to a process for the preparation of a particulate olefin polymerization catalyst component comprising a magnesium dihalide, a titanium tetrahalide and a carboxylic acid ester. The invention also relates to such a catalyst component and its use for the polymerisation of olefins.

**Background of the invention**

10 The process for the preparation of a particulate olefin polymer catalyst component as described in the applicant's patent applications FI 981717 and FI 981718 which were not public when present application was filed, includes a step in which a fraction of a magnesium dihalide-titanium tetrahalide-carboxylic acid ester complex is recovered by precipitation from solution. This precipitation is traditionally made by contacting the solution with a large amount of an aliphatic hydrocarbon.  
15 However, such precipitation leads to a tar-like reaction product of low catalytic activity, that need to be washed several times in order to decrease the amount of unactive titanium complex. Such washing leads to a further decreased activity of the catalyst.

20 Aromatic hydrocarbons have also been used for the precipitation, but they lead to a very finely divided precipitate which is difficult to deposit.

**Description of the invention**

The purpose of the present invention is to provide a fast process which results in a catalyst component having good activity. This has now been reached by a novel process for the preparation of a catalyst component of the above type, which is  
25 mainly characterised by the steps of  
(i) reacting in solution a magnesium compound containing an alkoxy group, a carboxylic acid halide and a four-valent titanium compound containing a halogen, for obtaining a dissolved reaction product and  
(ii) recovering a fraction of the reaction product from step (i) in particulate form  
30 by contacting the dissolved reaction product with a mixture of an aromatic and an aliphatic hydrocarbon, or by contacting the dissolved reaction product first with an aromatic hydrocarbon and then with an aliphatic hydrocarbon, the amount of aromatic and aliphatic hydrocarbon being at least 5 mol per mol of magnesium.

The components of step (i) can be added in any order, however a preferred embodiment of the invention is characterised in that in a first step of step (i), the magnesium compound containing an alkoxy group is reacted with the carboxylic acid halide in the presence of a first solvent and in a second step of step (i) the  
5 obtained product is further reacted with the four-valent titanium compound containing a halogen in the presence of a second solvent.

It has thus been found that a fast process for the preparation of a particulate olefin polymerization catalyst component having good activity and comprising a magnesium dihalide, a titanium tetrahalide and a carboxylic acid can be reached by  
10 using a mixture of an aromatic hydrocarbon and an aliphatic hydrocarbon for the recovering of a fraction of the reaction product. The fraction has an optimal composition and preferably leads to the catalyst component  $(\text{MgCl}_2)_{6-12} \cdot \text{TiCl}_4 \cdot \text{carboxylic acid ester}$  which is catalytically very active.

The catalyst component recovered in step (i) is preferably obtained in solid form by  
15 precipitation. Precipitation in the present invention means that the reaction product formed in solution is recovered as a powder, the particles of which consist of similar individual molecules of that reaction product. The particles formed according to the present invention are thus homogeneous.

According to a preferable embodiment of the invention, the recovering stage is  
20 performed by contacting the dissolved reaction product of step (i) with from 5 to 5000 mol, preferably from 10 to 2000 mol, most preferably from 20 to 1000 mol per mol of magnesium of said hydrocarbon mixture.

Said hydrocarbon mixture of step (ii) is preferably a mixture of an aromatic hydrocarbon and an aliphatic hydrocarbon, which mixture preferably contains from 95 to  
25 40%, most preferably from 90 to 50% by weight of an aromatic hydrocarbon and from 5 to 60%, most preferably from 10 to 50% by weight of an aliphatic hydrocarbon.

The aromatic hydrocarbon used in the process is preferably selected from substituted and unsubstituted benzenes, preferably from alkylated benzenes, more  
30 preferably from toluene and the xylenes, most preferably from toluene. The aliphatic hydrocarbon is preferably selected from aliphatic  $\text{C}_5\text{-C}_{12}$ -hydrocarbons, preferably from pentane, hexane, heptane and/or octane, most preferably from pentane, hexane or heptane.

According to another embodiment of the invention, the recovering of the reaction product in particulate form is performed by precipitating the dissolved reaction product with an aromatic hydrocarbon and settling the precipitate by gradually adding aliphatic hydrocarbon to the precipitated reaction mixture. This recovering is performed by contacting said dissolved reaction product with from 95 to 40%, preferably from 90 to 50% by weight of the total amount of hydrocarbons added in the recovering step (ii) of said aromatic hydrocarbon, and that said settling of the precipitate is performed by adding from 5 to 60%, preferably from 10 to 50% by weight of the total amount of hydrocarbons added in the recovering step (ii) of said aliphatic hydrocarbon.

According to a preferred embodiment of the invention, the recovered fraction of the reaction product which has been obtained in particulate form is washed at least once, preferably at least twice, most preferably at least three times with a hydrocarbon, which preferably is selected from aromatic and aliphatic hydrocarbons.

It is preferable if said recovered catalyst component is washed with toluene, preferably with hot (e.g. 90 °C) toluene. It is further preferable if said recovered catalyst component is washed with heptane, most preferably with hot (e.g. 90 °C) heptane. Yet further, it is preferable if said recovered catalyst component is washed with pentane. A washing step typically includes several substeps. Such a washing sequence is, for example, one wash with toluene at 90 °C, two washes with heptane at 90 °C and one or two washes with pentane at room temperature.

The washing can according to the invention be optimized to give a catalyst with novel and desirable properties. Finally, the washed catalyst component is usually dried, preferably by evaporation.

When titanium tetrachloride is used as titanium tetrahalide in step (i), the solvent in this step can be an excess of titanium tetrachloride or a mixture thereof with a hydrocarbon.

The molar ratio of said first solvent in step (i) to magnesium is preferably less than 10. According to an embodiment of the invention, the molar ratio of said solvent to magnesium is from 4 to 10, preferably from 5 to 9 and most preferably from 6 to 8.

Further, in step (i), the first solvent used is preferably an aliphatic C<sub>5</sub>-C<sub>12</sub>-hydrocarbon, preferably pentane, hexane, heptane and/or octane, most preferably pentane, hexane or heptane, which before reacting the titanium compound in a second step is replaced in the reaction mixture by an aromatic hydrocarbon. This means e.g. that

the alkoxy magnesium compound may initially be reacted with the acid halide in an aliphatic hydrocarbon, after which the aliphatic hydrocarbon is replaced by an aromatic hydrocarbon before reacting further with the titanium halide.

- 5      Optionally, the first solvent is an aromatic hydrocarbon selected from substituted, unsubstituted and alkylated benzenes, preferably from alkylated benzenes, more preferably from toluene and the xylenes, most preferably from toluene, whereby the first solvent can be used as the second solvent in step (i).

- 10     The molar ratio of said second solvent to magnesium is preferably from 3 to 10, more preferably from 4 to 8 and most preferably from 5 to 7. Said second solvent is preferably an aromatic hydrocarbon, selected from substituted, unsubstituted and alkylated benzenes, preferably from alkylated benzenes, more preferably from toluene and the xylenes, most preferably from toluene.

- 15     It is preferable if the intermediates as well as the final product of the claimed process are distinct compounds with an essentially stoichiometric composition. Often, they are complexes. A complex is, according to Römpps Chemie-Lexicon, 7. Edition, Franckh'sche Verlagshandlung, W. Keller & Co., Stuttgart, 1973, page 1831, "a derived name of *compounds of higher order*, which originate from the combination of *molecules*, - unlike compounds of first order, in the creation of which atoms participate".

- 20     The magnesium compound containing an alkoxy group is preferably selected from the group consisting of magnesium dialkoxides, complexes of a magnesium dihalide and an alcohol, and complexes of a magnesium dihalide and a magnesium dialkoxide. It may be a reaction product of an alcohol and a magnesium compound selected from the group consisting of dialkyl magnesiums, alkyl magnesium  
25     alkoxides, alkyl magnesium halides and magnesium dihalides. It can further be selected from the group consisting of dialkyloxy magnesiums, diaryloxy magnesiums, alkyloxy magnesium halides, aryloxy magnesium halides, alkyl magnesium alkoxides, aryl magnesium alkoxides and alkyl magnesium aryloxides.

- 30     Typical magnesium dialkoxides are magnesium dibutoxide and magnesium dipentoxide. The preferred magnesium dihalide to be reacted is magnesium dichloride  $MgCl_2$ . The dialkyl magnesium to be reacted has the formula  $R_2Mg$ , wherein each one of the two R:s is a similar or different  $C_1$ - $C_{20}$  alkyl, preferably a similar or different  $C_4$ - $C_{10}$  alkyl. Typical magnesium alkyls are ethylbutyl magnesium, dibutyl magnesium, dipropyl magnesium, propylbutyl magnesium,

dipentyl magnesium, butylpentylmagnesium, butyloctyl magnesium and dioctyl magnesium. Most preferably, one R of the formula  $R_2Mg$  is a butyl group and the other R is an octyl group, i.e. the dialkyl magnesium compound is butyl octyl magnesium.

- 5 Typical alkyl-alkoxy magnesium compounds  $RMgOR$ , when used, are ethyl magnesium butoxide, butyl magnesium pentoxide, octyl magnesium butoxide and octyl magnesium octoxide.

The dialkyl magnesium, alkyl magnesium alkoxide or magnesium dihalide is most preferably reacted with a polyhydric alcohol  $R'(OH)_m$  or a mixture thereof with a  
10 monohydric alcohol  $R'OH$ . The use of a polyhydric alcohol  $R'(OH)_m$  improves both the activity and the morphology of the catalyst component compared to the use of a monohydric alcohol alone.

Typical polyhydric alcohols are ethylene glycol, propylene glycol, trimethylene glycol, 1,2-butylene glycol, 1,3-butylene glycol, 1,4-butylene glycol, 2,3-butylene  
15 glycol, 1,5-pentanediol, 1,6-hexanediol, 1,8-octanediol, pinacol, diethylene glycol, triethylene glycol, glycerol, trimethylol propane and pentareythritol. The polyhydric alcohol can be selected on the basis of the activity and morphology it gives the catalyst component. E.g. larger particle size and broader particle size distribution can be obtained by using ethylene glycol.

20 Typical  $C_1$ - $C_5$  monohydric alcohols are methanol, ethanol, n-propanol, iso-propanol, n-butanol, iso-butanol, sec.butanol, tert.butanol, n-amyl alcohol, iso-amyl alcohol, sec.amyl alcohol, tert.amyl alcohol, diethyl carbinol, akt. amyl alcohol, sec. isoamyl alcohol, tert.butyl carbinol. Typical  $C_6$ - $C_{10}$  monohydric alcohols are hexanol, 2-ethyl-1-butanol, 4-methyl-2-pentanol, 1-heptanol, 2-heptanol, 4-  
25 heptanol, 2,4-dimethyl-3-pentanol, 1-octanol, 2-octanol, 2-ethyl-1-hexanol, 1-nonanol, 5-nonanol, diisobutyl carbinol, 1-decanol and 2,7-dimethyl-2-octanol. Typical  $>C_{10}$  monohydric alcohols are n-1-undecanol, n-1-dodecanol, n-1-tridecanol, n-1-tetradecanol, n-1-pentadecanol, 1-hexadecanol, n-1-heptadecanol and n-1-octadecanol. The monohydric alcohols may be unsaturated, as long as they do  
30 not act as catalyst poisons.

Preferable monohydric alcohols are those of formula  $R'OH$  in which  $R'$  is a  $C_2$ - $C_{16}$  alkyl group, most preferably a  $C_4$ - $C_{12}$  alkyl group, like 2-ethyl-1-hexanol.

Preferably, essentially all of the carboxylic acid ester is a reaction product of the above mentioned carboxylic acid halide. The carboxylic acid halide is preferably a

dicarboxylic acid dihalide, more preferably an unsaturated  $\alpha,\beta$ -dicarboxylic acid dihalide, most preferably phthalic acid dichloride.

According to yet another embodiment of the invention, the four-valent titanium compound containing a halogen is a titanium tetrahalide  $TiX''_4$ , wherein  $X''$  is a  
5 halogen. Equivalent with said titanium tetrahalide is the combination of an alkoxy titanium halide and a halogenation agent thereof, which are able to form a titanium tetrahalide *in situ*. However, the most preferred titanium tetrahalide is titanium tetrachloride.

The reaction conditions used in the claimed process may be varied according to the  
10 used reactants and agents.

In the invention, it was further found that the addition of at least one halogenated hydrocarbon during the process led to a further improved catalytic activity.

The halogenated hydrocarbon preferably has the formula  $R'''X'''_n$  wherein  $R'''$  is an  $n$ -valent  $C_1$ - $C_{20}$  hydrocarbyl group,  $X'''$  is a halogen and  $n$  is an integer from 1 to 4.

15 Such chlorinated hydrocarbons are, e.g., monochloromethane, dichloromethane, trichloromethane (chloroform), tetrachloromethane, monochloroethane, (1,1)-dichloroethane, (1,2)-dichloroethane, (1,1,1)-trichloroethane, (1,1,2)-trichloroethane, (1,1,1,2)-tetrachloroethane, (1,1,2,2)-tetrachloroethane, pentachloroethane, hexachloroethane, (1)-chloropropane, (2)-chloropropane, (1,2)-dichloropropane,  
20 (1,3)-dichloropropane, (1,2,3)-trichloropropane, (1)-chlorobutane, (2)-chlorobutane, isobutyl chloride, tert.butyl chloride, (1,4)-dichlorobutane, (1)-chloropentane, (1,5)-dichloropentane. The chlorinated hydrocarbons of the invention may also be unsaturated, provided that the unsaturation does not act as catalyst poison in the final catalyst component.

25 In said halogenated hydrocarbon having the above formula,  $R'''$  is preferably a mono-or bivalent  $C_1$ - $C_{10}$  alkyl group, independently,  $X'''$  is preferably chlorine and, independently,  $n$  is preferably 1 or 2. Preferably said halogenated hydrocarbyl is a butyl chloride (BuCl) or a dichloroalkane like (1,4)-dichlorobutane, more preferably tertiary butyl chloride or a dichloroalkane like (1,4)-dichlorobutane, most preferably  
30 a dichloroalkane like (1,4)-dichlorobutane.

In addition to the above described process, the invention also relates to a particulate olefin polymerization catalyst component comprising a magnesium dihalide, a



titanium tetrahalide and a carboxylic acid ester as internal electron donor, which has been prepared according to the above described process.

- 5 In addition to the above described process and catalyst component, the invention also relates to a process for the polymerisation of olefins, wherein an olefin is contacted with a particulate olefin polymerization catalyst component comprising a magnesium dihalide, a titanium tetrahalide and a carboxylic acid ester as internal electron donor, and an organometallic cocatalyst, which has been prepared according to the above described process. Preferably, the organometallic cocatalyst is an alkyl aluminium chloride.

- 10 The invention is described below by means of examples, the purpose of which is merely to illustrate the invention.

### Examples

#### Preparation of the catalyst components

##### Example 1

- 15 0.25 mol of ethylene glycol was added to 0.25 mol of 2-butyl-2-ethyl-1,3-propanediol in an inert reactor at room temperature. Further, 2 mol of 2-ethyl-1-hexanol was added and the reaction mixture was rapidly heated to 60 °C to increase the dissolution and the mixture was allowed to cool to 20 °C.

- 20 1 mol of 20% butyl octyl magnesium in heptane was added at room temperature and the mixture was heated at 60 °C for 30 minutes. 0,5 mol of 1,2-phthalic acid dichloride at 60 °C was added to the reaction mixture and the heating at 60 °C was continued for 30 minutes, after which 1,1 mol of butyl chloride was added at 60 °C and the reaction mixture was heated at 60 °C for 20 minutes.

- 25 After the heating, the solvent was evaporated at 105° under nitrogen flow during approximately 90 minutes. 5 mol toluene was added at 90 °C and the reaction mixture was heated during 10 minutes. The cold solution obtained was siphonated into a solution of 7 mol of titanium tetrachloride at 110 °C.

- 30 The solution was then heated at 110 °C for 5 minutes and the reaction product was recovered by adding 72 ml of toluene and 30 ml of heptane at 90 °C and allowing it to settle for 30 minutes.

After the recovering, the reaction product was washed five times: first with 102 ml of toluene at 90 °C for 4 minutes, secondly with 98 ml of heptane at 90 °C for 2 minutes, thirdly with 122 ml of heptane at 90 °C for 2 minutes, fourthly with 126 ml of pentane at 20 °C for 2 minutes and fifthly with 105 ml of pentane at 20 °C for 2 minutes. The settling in volume of the catalyst precipitation (in ml) during the recovery and the washings are summarised in Table 1. The reaction product was dried under nitrogen flow at 60° for 45 minutes. The yield was 4.2 g.

**Table 1. Settling of the reaction product**

Settling time (min)	Recovery	Washings				
	Toluene/ heptane	Toluene/1	Heptane/1	Heptane/2	Pentane/1	Pentane/2
0	150	140	137	147	144	122
1	37	75	23	21	19	19
2	34	40	19	18	17	17
3	30	30				
4	28	28				
5	27					

## 10 Example 2

The same procedure as in example 1 was used for the preparation of the magnesium complex. The cold solution obtained was siphonated into a solution of 7 mol of titanium tetrachloride at 110 °C.

The solution was then heated at 110 °C for 5 minutes and the reaction product was recovered by adding 60 ml of toluene and 40 ml of heptane at 90 °C and allowing it to settle for 49 minutes.

After the recovering, the reaction product was washed five times: first with 199 ml of toluene at 90 °C for 2 minutes, secondly with 146 ml of heptane at 90 °C for 2 minutes, thirdly with 129 ml of heptane at 90 °C for 1 minute, fourthly with 126 ml of pentane at 20 °C for 1 minute and fifthly with 117 ml of pentane at 20 °C for 1 minute. The settling in volume of the catalyst precipitation (in ml) during the recovery and the washings are summarised in Table 2. The reaction product was dried under nitrogen flow at 60° for 50 minutes. The yield was 4.2 g.

**Table 2. Settling of the reaction product**

Settling time (min)	Recovery	Washings				
	Toluene/ heptane	Toluene/1	Heptane/1	Heptane/2	Pentane/1	Pentane/2
0	150	125	175	155	140	130
1	19	50	20	18	16	14
2	17	16	15	14	13	13

**Example 3**

5 The same procedure as in example 1 was used for the preparation of the magnesium complex. The cold solution obtained was siphonated into a solution of 7 mol of titanium tetrachloride at 110 °C.

The solution was then heated at 110 °C for 5 minutes and the reaction product was recovered by adding consecutively 74 ml of toluene and 30 ml of heptane at 90 °C and allowing it to settle for 5 minutes.

10 After the recovering, the reaction product was washed five times: first with 113 ml of toluene at 90 °C for 5 minutes, secondly with 119 ml of heptane at 90 °C for 2 minutes, thirdly with 143 ml of heptane at 90 °C for 2 minutes, fourthly with 120 ml of pentane at 20 °C for 2 minutes and fifthly with 112 ml of pentane at 20 °C for 2 minutes. The settling in volume of the catalyst precipitation (in ml) during the  
15 recovery and the washings are summarised in Table 3. The reaction product was dried under nitrogen flow at 60° for 45 minutes. The yield was 4.4 g.

**Table 3. Settling of the reaction product**

Settling time (min)	Recovery	Washings				
	Toluene/ heptane	Toluene/1	Heptane/1	Heptane/2	Pentane/1	Pentane/2
0	160	160	155	170	138	131
1	45	35	24	20	22	21
2	38	28	20	18	19	16
3	37	25				
4	36	24				
5	35	23				

**Comparative example 4**

The same procedure as in example 1 was used for the preparation of the magnesium complex. The solution obtained, at 110 °C, was siphonated into a hot solution of 10 mol of titanium tetrachloride.

- 5 The solution was then heated at 110 °C for 5 minutes and the reaction product was recovered by adding 111 ml of toluene at 90 °C and allowing it to settle for 30 minutes.

After the recovering, the reaction product was washed four times: first with 160 ml of toluene at 90 °C for 28 minutes, secondly with 160 ml of heptane at 90 °C for 8 minutes, thirdly with 150 ml of heptane at 90 °C for 6 minutes and fourthly with 150 ml of pentane at 20 °C for 6 minutes. The settling in volume of the catalyst precipitation (in ml) during the recovery and the washings are summarised in Table 4. The reaction product was dried under nitrogen flow at 60° for 30 minutes. The yield was 6.6 g.

15 **Table 4. Settling of the reaction product**

Settling time (min)	Recovery Toluene	Washings Toluene/1	Heptane/1	Heptane/2	Pentane
0	175	240	220	200	185
10	95	80	48	37	36
20	70	56			
30	65	52			

**Chemical characterisation of the catalyst components**

20 The catalyst components were characterised with respect to their chemical composition by measuring their Mg, Ti and Cl content. The Mg and Ti analysis was started by dissolving the samples in a mixture of nitric and hydrofluoric acid. The metal was measured by flame atomic absorption with a nitrous oxide/acetylene flame. Chloride was determined after dissolution in dilute sulphuric acid by potentiometric titration with a standard silver nitrate solution. The results are summarised in Table 5.

- 25 The determination of the phthalic esters (DOP) and the phthalic anhydride (PA) were done by first dissolving the sample in acetone. The dissolution was facilitated by

keeping the acetone slurry in an ultra-sound bath for 5 minutes. After this the samples were filtered and run by solution chromatography. Each component was identified by comparing the respective retention time and UV spectra with standard conditions.

5 **Table 5. Chemical characteristics of the catalyst components**

Catalyst	Example 1	Example 2	Example 3	Comp. ex. 4
Mg (wt-%)	13.8	14.1	14.3	10.3
Mg/Ti (mol/mol)	7.0	8.4	7.0	3.3
Ti (wt-%)	3.9	3.3	4.0	6.2
Ti (mol)	1.0	1.0	1.0	1.0
Cl (wt-%)	50.5	57.5	53.6	44.8
DOP (wt-%)	19.4	16.5	20.6	27.4
DOP/Ti (mol/mol)	0.6	0.6	0.6	0.5
PA (wt-%)	0.61	0.88	0.58	0.53

#### Bulk polymerization of propene

10 Propene was polymerised in a stirred tank reactor having a volume of 5 l. About 0.9 ml of triethyl aluminium (TEA) as cocatalyst, about 0.12 ml of a 100-% solution of cyclohexyl dimethoxy silane (CMMS) as an external donor and 30 ml of n-pentane were mixed and allowed to react for 5 minutes. Half of the mixture was added to the polymerisation reactor and the other half was mixed with about 20 mg of catalyst complex, prepared in examples 1-4, respectively. After additional 5 minutes the catalyst/TEA/donor/n-pentane mixture was introduced to the reactor.

15 The Ti/Al molar ratio was 250 and the Al/external donor molar ratio was 10. 70mmol of hydrogen and 1400 g of propene were introduced to the reactor and the temperature was risen to 70 °C.

20 The polymerisation time was 60 minutes (at 70 °C), after which the polymer formed was taken out from the reactor and characterised with respect to their melt flow rate (MFR<sub>2</sub>, in g/10 min), determined according to the standard ISO 1133 (230 °C and 2.16 kg load) and bulk density (BD). Activity (Activ.) is given in g of polypropene (PP) formed per g of catalyst or per g of Ti. The results are summarised in Table 6.

**Table 6. Polymerisation results**

Catalyst	Example 1	Example 2	Example 3	Comp. ex. 4
Activ. (kgPP/g*cat)	24.2	23.7	27.0	16.9
Activ. (kgPP/g*Ti)	61.9	718	674	273
MFR <sub>2</sub>	5.0	5.2	4.9	5.2
BD (kg/m <sup>3</sup> )	290	446	345	280

## Claims

1. A process for the preparation of a particulate olefin polymerization catalyst component comprising a magnesium dihalide, a titanium tetrahalide and a carboxylic acid ester, **characterised** by the steps of
  - 5 (i) reacting in solution a magnesium compound containing an alkoxy group, a carboxylic acid halide and a four-valent titanium compound containing a halogen, for obtaining a dissolved reaction product and
  - (ii) recovering a fraction of the reaction product from step (i) in particulate form by contacting the dissolved reaction product with a mixture of an aromatic and an aliphatic hydrocarbon, or by contacting the dissolved reaction product first with an aromatic hydrocarbon and then with an aliphatic hydrocarbon, the amount of aromatic and aliphatic hydrocarbon being at least 5 mol per mol of magnesium.
2. A process according to claim 1, **characterised** in that in a first step of step (i), the magnesium compound containing an alkoxy group is reacted with the carboxylic acid halide in the presence of a first solvent and in a second step of step (i) the obtained product is further reacted with the four-valent titanium compound containing a halogen in the presence of a second solvent.
3. A process according to claim 2, **characterised** in that the first solvent is an aliphatic C<sub>5</sub>-C<sub>12</sub>-hydrocarbon, preferably pentane, hexane, heptane and/or octane, most preferably pentane, hexane or heptane.
4. A process according to claim 3, **characterised** in that the first solvent is an aromatic hydrocarbon, selected from substituted, unsubstituted and alkylated benzenes, preferably from benzene, toluene and the xylenes, most preferably from toluene.
5. A process according to claim 3 or 4, **characterised** in that the molar ratio of said first solvent to magnesium is from 4 to 10, preferably from 5 to 9, most preferably from 6 to 8.
6. A process according to any of claims 2-5, **characterised** in that the second solvent is an aromatic hydrocarbon, selected from substituted, unsubstituted and alkylated benzenes, preferably from benzene, toluene and the xylenes, most preferably from toluene.

7. A process according to claim 6, characterised in that the molar ratio of said second solvent to magnesium is from 3 to 10, preferably from 4 to 8, most preferably from 5 to 7.
8. A process according to claim 2, characterised in that the first and the second  
5 solvents are the same aromatic hydrocarbon, selected from substituted, unsubstituted and alkylated benzenes, preferably from benzene, toluene and the xylenes, most preferably from toluene.
9. A process according to claim 8, characterised in that the molar ratio of said solvent to magnesium is from 3 to 10, preferably from 4 to 8, most preferably from  
10 5 to 7.
10. A process according to any of claims 2-9, characterised in that the first solvent is an aliphatic C<sub>5</sub>-C<sub>12</sub>-hydrocarbon, preferably pentane, hexane, heptane and/or octane, most preferably pentane, hexane or heptane, which is replaced by an aromatic hydrocarbon before the second step.
11. A process according to claim 1, characterised in that the mixture of an  
15 aromatic hydrocarbon and an aliphatic hydrocarbon in step (ii) contains from 95 to 40%, preferably from 90 to 50% by weight of an aromatic hydrocarbon and from 5 to 60%, preferably from 10 to 50% by weight of an aliphatic hydrocarbon.
12. A process according to claim 11, characterised in that the aromatic hydro-  
20 carbon is selected from substituted, unsubstituted and alkylated benzenes, preferably from alkylated benzenes, more preferably from toluene and the xylenes, most preferably from toluene.
13. A process according to claim 11 or 12, characterised in that the aliphatic hydrocarbon is an aliphatic C<sub>5</sub>-C<sub>12</sub>-hydrocarbon, preferably pentane, hexane,  
25 heptane and/or octane, most preferably pentane, hexane or heptane.
14. A process according to claim 1, characterised in that the recovering of a fraction of the reaction product in particulate form is performed by contacting the dissolved reaction product with from 5 to 5000 mol, preferably from 10 to 2000 mol, most preferably from 20 to 100 mol per mol of magnesium of said  
30 mixture of an aromatic and an aliphatic hydrocarbon.
15. A process according to any preceding claim, characterised in that the recovering of the reaction product in particulate form is performed by precipitating



the dissolved reaction product with an aromatic hydrocarbon and settling the precipitate by gradually adding aliphatic hydrocarbon to the precipitated reaction mixture.

- 5 16. A process according to claim 15, characterised in that said dissolved reaction product is contacted with from 95 to 40%, preferably from 90 to 50% by weight of the total amount of hydrocarbons added in the recovering step (ii) of said aromatic hydrocarbon, and that said settling of the precipitate is performed by adding from 5 to 60%, preferably from 10 to 50% by weight of the total amount of hydrocarbons added in the recovering step (ii) of said aliphatic hydrocarbon.
- 10 17. A process according to any preceding claim, characterised in that the recovered fraction of the reaction product which has been recovered in particulate form is washed at least once, preferably at least twice, most preferably at least three times with a hydrocarbon, which preferably is selected from aromatic and aliphatic hydrocarbons.
- 15 18. A process according to any preceding claim, characterised in that the magnesium compound containing an alkoxy group is selected from the group consisting of magnesium dialkoxides, complexes of a magnesium dihalide and an alcohol, and complexes of a magnesium dihalide and a magnesium dialkoxide.
- 20 19. A process according to any preceding claim, characterised in that the magnesium compound containing an alkoxy group is a reaction product of an alcohol and a magnesium compound selected from the group consisting of dialkyl magnesiums, alkyl magnesium alkoxides, alkyl magnesium halides and magnesium dihalides.
- 25 20. A process according to claim 19, characterised in that the magnesium compound is a dialkyl magnesium, preferably a di-C<sub>4</sub>-C<sub>10</sub> alkyl magnesium.
21. A process according to claim 19 or 20, characterised in that the magnesium compound is a magnesium dihalide, preferably magnesium dichloride.
- 30 22. A process according to any preceding claim, characterised in that the alcohol is selected from the group consisting of polyhydric alcohols and mixtures of a monohydric alcohol and a polyhydric alcohol.

23. A process according to claim 22, characterised in that the polyhydric alcohol is a glycol or glycerol, preferably ethylene glycol, 2-butyl-2-ethyl-1,2-propanediol or glycerol.
24. A process according to any preceding claim, characterised in that essentially  
5 all of the carboxylic acid ester is a reaction product of the carboxylic acid halide.
25. A process according to any preceding claim, characterised in that the carboxylic acid halide is a dicarboxylic acid dihalide, preferably an unsaturated  $\alpha,\beta$ -dicarboxylic acid dihalide, most preferably phthalic acid dichloride.
26. A process according to any preceding claim, characterised in that the four-  
10 valent titanium compound containing a halogen is a titanium tetrahalide, preferably titanium tetrachloride.
27. A process according to any preceding claim, characterised in that during the reaction of the magnesium compound containing an alkoxy group and the carboxylic acid halide, a halogenated hydrocarbon is added to the reaction mixture.
- 15 28. A particulate olefin polymerization catalyst component comprising a magnesium dihalide, a titanium tetrahalide and a carboxylic acid ester as internal electron donor, characterised in that it has been prepared according to any of claims 1-27.
- 20 29. Process for the polymerisation of olefins, wherein an olefin is contacted with a particulate olefin polymerization catalyst component comprising a magnesium dihalide, a titanium tetrahalide and a carboxylic acid ester as internal electron donor, and an organometallic cocatalyst, characterised in that said particulate olefin polymerisation catalyst component has been prepared according to any of claims 1-28.
- 25 30. Process according to claim 29, characterised in that the organometallic cocatalyst is an alkyl aluminium chloride.

## INTERNATIONAL SEARCH REPORT

International application No.

PCT/FI 00/00409

## A. CLASSIFICATION OF SUBJECT MATTER

IPC7: C08F 4/654, C08F 10/00

According to International Patent Classification (IPC) or to both national classification and IPC

## B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)

IPC7: C08F

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practicable, search terms used)

## C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
A	WO 9736938 A1 (BOREALIS A/S), 9 October 1997 (09.10.97)  --	1-30
A	EP 0173472 A2 (TOA NENRYO KOGYO KABUSHIKI KAISHA), 5 March 1986 (05.03.86)  --	1-30
P, A	EP 0926165 A1 (BOREALIS A/S), 30 June 1999 (30.06.99)  -----	1-30

☐ Further documents are listed in the continuation of Box C.☒ See patent family annex.

## \* Special categories of cited documents:

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\*&\* document member of the same patent family

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**INTERNATIONAL SEARCH REPORT**

Information on patent family members

08/05/00

International application No.

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